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Solid-phase microextraction with pH adjustment for the determination of aromatic acids and bases in water

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Abstract

Adjusting the pH of water samples before performing solid-phase microextraction (SPME) analysis can be used to selectively extract organic acids (at pH 2) and bases (at pH 12). Sorption behavior of test organics is predictable based on the acid dissociation constant in water. In general, polyacrylate (PA) and Carbowax–divinylbenzene (CW–DVB) show substantially higher fiber/water sorption coefficients (K_d values) than a polydimethylsiloxane (PDMS) coated fiber. Gas chromatography–flame ionization detection (GC–FID) detection limits with the CW–DVB sorbent are ~0.5 to 10 ng/ml in a 2-ml water sample for a variety of aromatic amines, phenols, and chlorinated phenols, and are ~1 to 50 ng/ml for the same solutes using the PA sorbent. However, the PA fiber is more selective (depending on the water pH) for the acid or base components than the CW–DVB fiber. With proper pH adjustment, the recovery of spiked aromatic amines and phenols from a surface wetlands water ranged from 73 to 118% of the known values, with a precision (R.S.D.) of ~5 to 20%. SPME quantitation of phenols in a coal gasification wastewater using a PA fiber also gave excellent agreement with conventional methylene chloride extraction, although continued use of a single fiber with this wastewater led to poorer precision.

Keywords: Solid-phase microextraction; Extraction methods; Water analysis; Environmental analysis; Organic acids; Phenols; Anilines; Amines; Phenathridine; Quinoline

1. Introduction

Solid-phase microextraction (SPME) has been particularly successful for the determination of non-polar organics in water such as fuel components, polycyclic aromatic hydrocarbons (PAHs), and poly-chlorinated biphenyls (PCBs) [1–5]. The recent development of SPME fibers having more polar sorbents, as well as in situ derivatization techniques, have also increased the ability of SPME to determine more polar organics such as many pesticides, phenols and other organic acids, and aliphatic amines [6–17], although the addition of a derivatization step complicates the overall method. Ideally, SPME determinations of organic acids and bases will be performed without the need for derivatization procedures, especially if the target species can be analyzed by gas chromatography (GC) without derivatization.

In addition to using more polar sorbent materials, adding acid to a water sample has been demonstrated to increase the SPME/water partition coefficient (K_d) for phenols, and thus increase the analytical

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sensitivity of the method [17,18]. However, in most studies to date, no attempt has been made to control the water pH during the SPME sorption step, despite the fact that many organic acids and bases have acid dissociation constants (pK_a) in the same general range as water samples (e.g., the pH of surface and ground water samples generally ranges from 5 to 8). For such species, relatively small changes in pH could dramatically affect their water/SPME distribution behavior by changing the effective concentration of the neutral (not ionized) species, and thus could lead to quantitative errors when the pHs of the sample and calibration waters are significantly different. In addition, buffering the pH of water samples could be used to increase selectivity of the SPME process, in a manner analogous to the conventional ''acid–base/neutral'' methylene chloride extraction method for water samples.

In the present study, the effect of water pH on the SPME sorption behavior of organic acids and bases is investigated in buffered solutions at pH values of 2, 7 and 12 using SPME fibers coated with three different stationary phases including polydimethylsiloxane (PDMS), polyacrylate (PA), and Carbowax–divinylbenzene (CW–DVB). K_d values at each pH are determined with each fiber using phenols and amines with acid dissociation constants (pK_a) ranging from ~10 to <1. The ability of pH control with SPME to selectively extract aromatic acids versus bases is demonstrated, and the methods developed are applied to surface and waste water samples.

2. Experimental

2.1. SPME sorbents

Three commercially-available fibers were used in this study including 100 μm PDMS, 85 μm PA and 65 μm CW–DVB. According to the supplier (Supelco, Bellefonte, PA, USA), the volumes of the sorbent phases were 0.612 μl (PDMS), 0.520 μl (PA) and 0.357 μl (CW–DVB) and these volumes were assumed to be correct for all K_d calculations. Before use, each fiber was conditioned in a heated GC injection port under helium flow at the conditions suggested by the supplier.

2.2. Standards and buffers

Aromatic acids and bases were chosen to represent a large range in pK_a values so that the dependence of SPME sorption behavior on water pH could be observed (Table 1). Standard solutions containing 1.00 mg/ml of each compound were prepared in acetone for spiking calibration water standards and the wetland water sample. Water standards for evaluating the three fibers were prepared by spiking 10 μl of the acetone solution into 1.9 ml of the appropriate buffered water in a 2-ml autosampler vial containing a PTFE-coated micro-stir bar (8 mm×1.5 mm diameter) for a final concentration of ~5 μg/ml for each test species. Buffers were: pH 2.00 (KCl–HCl, Fisher Chemical, USA), pH 7.00 (KH_2PO_4–NaOH, Fisher Chemical), and pH 12.00 (Na_2HPO_4–NaOH, LabChem, Pittsburgh, PA, USA) and used as received.

2.3. Fiber desorptions and GC determinations

All GC separations were performed with a Hewlett-Packard 5890 Series II GC system equipped with flame ionization detection (FID), a conventional split/splitless injection port, and an on-column in-

Table 1
Ambient water solubilities and pK_a for test organic acids and bases

Compound	pK_a[a]	Solubility at 25°C (mg/l)
Bases		
Tributylamine	10[b]	–[c]
Phenanthridine	5.6	–
Aniline	4.6	354 000
Quinoline	4.9	60 000
2,6-Diethylaniline	–	–
Diphenylamine	0.8	840
2-Nitroaniline	−0.3	1.3
Acids		
Phenol	10	90 000
2-Nitrophenol	7.2	2500
2,3-Dichlorophenol	7.4	–
2,4,5-Trichlorophenol	6	1200
Pentachlorophenol	4.7	20

[a] Acid dissociation constants of the protonated (ionized) bases, and the neutral acids.
[b] Value is for triisopropylamine.
[c] Value not available.

jection port. All SPME desorptions were performed in the split/splitless injection port in the splitless mode using a narrow-bore injection port liner (2 mm I.D.), as was previously demonstrated to give the best chromatographic peak shapes [19]. Splitless solvent injections were performed using a conventional splitless liner. The on-column injection port was used for solvent injections of standard solutions to calibrate the FID response for K_d determinations as previously described [5]. According to the manufacturer, the upper temperature limits for the SPME desorptions were 280, 320 and 265°C, for the PDMS, PA and CW–DVB fibers, respectively. However, previous reports have demonstrated that these fibers can be used for short desorptions at significantly higher temperatures in order to improve the recoveries of less volatile species with no significant loss in fiber performance [4,5]. Initial comparisons of the suggested desorption temperatures with the 300°C desorption temperatures used in this study showed no significant changes in the blanks for the three fiber materials, and did not demonstrate loss in sorbent capacity. Therefore, all desorptions were performed with an injection port temperature of 300°C so that the three fibers could be compared directly. An additional 10-min cleaning step was applied to each fiber in a separate GC injection port after each sample desorption. In addition, each stir bar was rinsed in a few ml of acetone after each use to prevent contamination of subsequent samples.

All separations were performed using a 25 m× 0.33 mm I.D. HP-5 column with a 0.17 μm film thickness. The oven temperature for the standard solutions and the wetland water sample was 35°C (held for 1 min during the SPME desorption), followed by a temperature at 5°C/min to 130°C, then by a temperature ramp at 16°C to 180°C, then a ramp at 25°C to 300°C. The temperature program for the coal gasification wastewater was 40°C (held for 2 min) followed by a ramp at 10°C/min to 300°C. Verification of peak identities was performed using a Hewlett-Packard 5972 GC–mass spectrometry (MS) system and the same chromatographic conditions as used for GC–FID.

2.4. K_d determinations

Fiber/water sorption coefficients were determined at pH 2, 7 and 12 with each of the three test fibers. Details of the method used to determine K_d values are given in Ref. [5]. In short, the GC–FID response was calibrated with on-column solvent injections of several dilutions of the standard mix in acetone. Based on these calibrations, the mass of each test species in the SPME fiber was determined by the FID peak area (at least five replicates at each condition). Since the mass of each test species spiked into the water samples is known, K_d values (i.e., the concentration of each congener in the SPME phase divided by its concentration in the water after SPME sorption) are calculated from the mass of each species in the SPME fiber (based on the FID peak area), the fiber sorbent volume (listed above), the mass spiked into the water sample (minus the amount removed by the fiber), and the 1.9 ml water volume. Since both absorption and adsorption can contribute to solute recovery, the K_d values reported here are referred to as sorption coefficients.

2.5. Samples

A wetland water was collected from a shallow waterfowl production area near Larimore (ND, USA) and had a suspended solids content of ~0.2%. Aliquots (1.9 ml) were transferred to 2-ml autosampler vials containing a stir bar. The sample was spiked with 5 μg/ml of each solute (10 μl of the acetone standard), and the pH was adjusted to 2 (with HCl) or 12 (with NaOH). Since the coal gasification water was very highly contaminated with aromatic alcohols, it was acidified with HCl and diluted 1:50 in the pH 2 buffer before SPME analysis was performed on 1.9 ml aliquots placed in 2-ml autosampler vials as described above. SPME calibration for the coal gasification wastewater was achieved by spiking appropriate dilutions of an acetone solution of each of the phenolic species reported in the results from the wastewater analyses into 1.9 ml of the pH 2 buffer solution and analyzing in a manner identical to that used for the sample.

Conventional methylene chloride extraction of the coal gasification wastewater was performed using quadruplicate 2.0-ml aliquots of the undiluted water adjusted to pH 2 by the addition of 1.5 ml HCl (0.5 *M*). Each replicate was extracted four times with 2-ml aliquots of fresh methylene chloride. (A fifth

Table 2
Effect of pH on the fraction of acids removed from 1.9 ml of water with different fiber sorbents[a]

Compound	% Sorbed±S.D. at pH 2			% Sorbed±S.D. at pH 7		
	PDMS	PA	CW–DVB	PDMS	PA	CW–DVB
Phenol	0.11±0.07	0.50±0.06	0.60±0.20	0.09±0.05	0.68±0.10	0.51±0.17
2,3-Dichlorophenol	0.47±0.06	13±2	7.1±1	0.42±0.03	12±2	5.8±1.4
2-Nitrophenol	0.48±0.08	1.2±0.1	2.7±0.3	0.25±0.02	0.82±0.11	1.3±0.3
2,4,5-Trichlorophenol	2.7±0.24	81±9	35±2	–	62±8	25±4.5
Pentachlorophenol	31±1	86±7	55±2	0.44±0.03	10.0±0.7	11.0±0.6

[a] All values are based on five determinations. None of the acids were detected on any of the fibers with a water of pH of 12, except 2,4,5-trichlorophenol which showed 1.10±0.01% removal with the CW–DVB-coated fiber.

methylene chloride extraction was performed and analyzed separately, which demonstrated that the first four methylene chloride extractions quantitatively removed the phenols from the water samples). After combining the first four methylene chloride aliquots, 2.3 mg of 3,5-dichlorophenol was added as an internal standard and the extracts were analyzed by GC–FID.

3. Results and discussion

3.1. Effect of water pH and sorbent type

The initial evaluation of the effects of water pH and the fiber sorbent phase are given in Tables 2 and 3 which show the fraction of each analyte removed from a 5 μg/ml solution in 1.9 ml of water with a 30-min sorption step. For the organic acids (Table 2), the effect of pH on the sorption of a particular species is as expected based on its pK_a. For example, phenol has the highest pK_a (10) of the test compounds, and shows no significant change in the fraction sorbed to any of the fibers when the pH is changed from 7 to 2, in agreement with a previous report which used the PA fiber [17]. This would be expected since the phenol molecules are largely neutral at both pH values. However, when the pK_a of the test analyte lies between 2 and 7, the effect of pH on sorption of the species is large. For example, at a pH of 7, pentachlorophenol (pK_a of 4.7) is mostly ionized, while at a pH of 2, it is present mostly in the neutral form. Thus, the fraction of pentachlorophenol which is sorbed by all three sorbents increases nearly by an order of magnitude at pH 2 compared to pH 7.

Similar to earlier reports [17,18,20], the PA sorbent increased the sorption of all of the phenols significantly over the PDMS-coated fiber. Similar increases were found with the CW–DVB sorbent. However, none of the sorbents showed significant

Table 3
Effect of pH on the fraction of bases removed from 1.9 ml of water with different fiber sorbents[a]

Compound	% Sorbed±S.D. at pH 2			% Sorbed±S.D. at pH 7			% Sorbed±S.D. at pH 12		
	PDMS	PA	CW–DVB	PDMS	PA	CW–DVB	PDMS	PA	CW–DVB
Tributylamine	ND[b]	ND	ND	0.35±0.04	ND	0.19±0.06	36±6	16±1	10±2
Phenanthridine	0.12±0.07	0.10±0.005	1.8±0.2	7.1±0.19	18±0.30	14±1	5.4±0.89	15±1	15±1.3
Aniline	ND	ND	ND	ND	0.38±0.06	0.39±0.11	0.10±0.05	0.31±0.12	0.64±0.07
Quinoline	ND	ND	ND	0.55±0.04	ND	1.3±0.5	0.43±0.10	0.74±0.08	3.5±0.17
2,6-Diethylaniline	0.07±0.03	ND	0.53±0.08	1.7±0.13	3.9±0.9	4.4±0.94	1.5±0.33	3.8±0.37	6.0±0.28
Diphenylamine	8.3±0.6	29±5	18±0.4	9.5±0.34	36±5	20±2.32	9.1±2	35±4	19±1.9
2-Nitroaniline	0.17±0.02	2.1±0.2	3.0±0.3	0.17±0.01	2.9±0.3	2.4±0.4	0.18±0.03	2.5±0.3	3.8±0.1

[a] All values based on five determinations.
[b] ND=Not detected. Estimated % removals were <0.01%.

removal of the phenols at a water pH of 12 (except for the 1% sorption shown by the CW–DVB fiber for 2,4,5-trichlorophenol), as would be expected since all of the test phenols are essentially ionized at a pH of 12.

For the organic bases (Table 3), the sorption behavior also follows the pK_a values. (Note that the pK_a values are those for the dissociation of the protonated form of the base). For tributylamine (pK_a of 10), the pH had to be raised to pH 12 for any substantial sorption to be observed, as would be expected since tributylamine exists primarily as the ionized (protonated) form at the lower pH values tested. For the bases with pK_a values of ~5 (e.g., phenanthridine), little sorption is seen at a pH of 2. At higher pH values, sorption increases dramatically and the amounts sorbed at the pH 7 and 12 are very similar. For aniline and quinoline, raising the pH does increase their sorption, but the fraction removed is quite low at every condition. These results are similar to those shown in Table 2 for phenol, and would be expected since the water solubilities of all three of these compounds are very high (90, 350, and 60 g/l for phenol, aniline and quinoline, respectively), even as substantially neutral compounds at a water pH of 7. Similarly, when the pH of the water is adjusted such that the predominant species is neutral, (e.g., pH of 2 for the acids, and pH of 12 for the bases), the K_d values of the individual test species increase as their water solubility decreases, as would be expected based on simple partitioning considerations.

Two of the organic bases, 2-nitroaniline and diphenylamine, showed little or no effect of pH on their sorption, since they both exist primarily as the neutral species at all three pH values tested. Similar to the results for the phenols, the sorption of organic bases was increased substantially with the PA and CW–DVB sorbents over the sorption to the PDMS fiber.

Since the three fibers tested are not available in the same coating thicknesses, the use of ‘‘% sorbed’’ from a test solution was used to compare their characteristics in Tables 2 and 3 to allow these results to be directly related to the GC peak areas achieved during analysis. Using the sorbent volumes supplied by the manufacturer (0.612 μl for PDMS, 0.520 μl PA, and 0.357 μl for CW–DVB), unitless sorption coefficients were calculated as previously described [5] by the ratio of the concentration of the analytes in the fiber sorbent divided by the concentration of the analytes in the water sample (after SPME sorption). As shown in Tables 4 and 5, the sorption coefficients for the non-polar PDMS fiber were substantially lower than those found for the PA and CW–DVB fibers, but there were no substantial differences between the two more polar fibers.

As noted above, all sorption times in this study were performed with a 30-min exposure to the water in a rapidly-stirred vial since one goal of these investigations was to perform the sample extraction in a time compatible with the GC analysis time. Therefore, the K_d values reported in Tables 4 and 5 may be slightly lower than the true equilibrium sorption coefficients. However, Buchholz [17] previously reported for phenols similar to those used in our study that 15 min was sufficient to obtain equilibrium for the PDMS fiber, and 40 min was sufficient for a 95 μm PA fiber (while the fiber used in our study was 85 μm). Although the literature contains few K_d values for the organic acids and bases shown in Tables 4 and 5, our results show reasonably good agreement with previously reported values as shown in Table 6.

Table 4
Effect of water pH and sorbent on experimental sorption coefficients (K_d values) for organic acids (30-min sorption)

Compound	K_d values with PA-coated fiber			K_d values with CW–DVB-coated fiber			K_d values with PDMS-coated fiber		
	pH 2	pH 7	pH 12	pH 2	pH 7	pH 12	pH 2	pH 7	pH 12
Phenol	19	25	ND	33	28	ND	3	2.8	ND
2-Nitrophenol	46	30	ND	150	69	ND	15	7.9	ND
2,3-Dichlorophenol	540	520	ND	410	330	ND	15	13	ND
2,4,5-Trichlorophenol	16 000	6100	ND	2900	1800	61	85	13	ND
Pentachlorophenol	22 000	420	ND	6500	630	ND	1400	14	ND

Table 5
Effect of water pH and sorbent on experimental sorption coefficients (K_d values) for organic bases (30-min sorption)

Compound	K_d values with PA-coated fiber			K_d values with CW–DVB-coated fiber			K_d values with PDMS-coated fiber		
	pH 2	pH 7	pH 12	pH 2	pH 7	pH 12	pH 2	pH 7	pH 12
Tributylamine	ND	ND	728	ND	10	630	ND	11	1800
Phenanthridine	4.7	800	670	97	900	940	3.9	240	180
Aniline	ND	14	12	ND	21	35	ND	2.3	3.0
Quinoline	ND	ND	27	ND	71	200	ND	17	14
2,6-Diethylaniline	ND	150	140	29	250	340	2.2	53	47
Diphenylamine	1500	2100	2000	1200	1300	1300	280	330	310
2-Nitroaniline	80	110	96	160	130	210	5.2	5.3	5.8

3.2. Fiber coating choice: detection limit and selectivity

Based on the results shown in Tables 2–5, both the PA and CW–DVB fibers are clearly superior to the PDMS fiber, but there is no clear reason to choose between the PA and CW–DVB coatings. A comparison of the fiber blanks (i.e., new and used fibers exposed to clean water and analyzed in a manner identical to the water samples), showed no large differences in sorbent artifact peaks, although the CW–DVB fiber did tend to show more late-eluting artifacts in the GC–FID chromatogram, especially when the water was buffered to a pH of 2 as shown in Fig. 1. (Note that Fig. 1 also includes the test species spiked at 5 or 0.5 ng/ml. Unidentified peaks are artifacts from the fiber being tested). Similarly, problems with carryover between samples were minimal with both fibers using the cleaning procedure described in Section 2.3. Since neither sorbent had an apparent advantage, additional comparisons of the PA and CW–DVB coatings were made based on the GC–FID detection limits that could be achieved, and based on the selectivity of the two fibers for acids and bases at different pH values.

The GC–FID detection limits for the PA and CW–DVB fibers in water buffered to a pH of 2 (for the organic acids) and a pH of 12 (for the organic bases) are given in Table 7. Each detection limit was determined by performing SPME determinations with 1.9 ml water samples spiked at 0.5, 1, 5, 10, 50, 100 and 250 ng/ml. Detection limits were defined as the lowest concentration that reproducibly yielded a signal at least three-times higher than the surrounding chromatographic noise. Examples of the sample peaks considered to be detected are shown in Fig. 1 for both the PA and CW–DVB fibers.

As would be expected, the detection limit for both

Table 6
Comparison of K_d values with literature values

Compound	Fiber coating	pH	K_d	
			Measured	Literature
Phenol	PDMS (100 μm)	7[a]	2.8	1.3[b]
	PA (85 μm)	7	25	1.3[b], 24[c]
2-Nitrophenol	PDMS (100 μm)	7	7.9	4.8[b]
	PA (85 μm)	7	30	3.7[b], 18[c]
	PA (85 μm)	2	150	110[d]
Pentachlorophenol	PA (85 μm)	7	420	170[b], 190[c]

[a] The pH was not adjusted in Refs. [17,18], and is assumed to be ~6.5 based on dissolved carbon dioxide. The PA fiber coating was 95 μm in Ref. [17].
[b] Ref. [17].
[c] Ref. [18].
[d] Ref. [20].

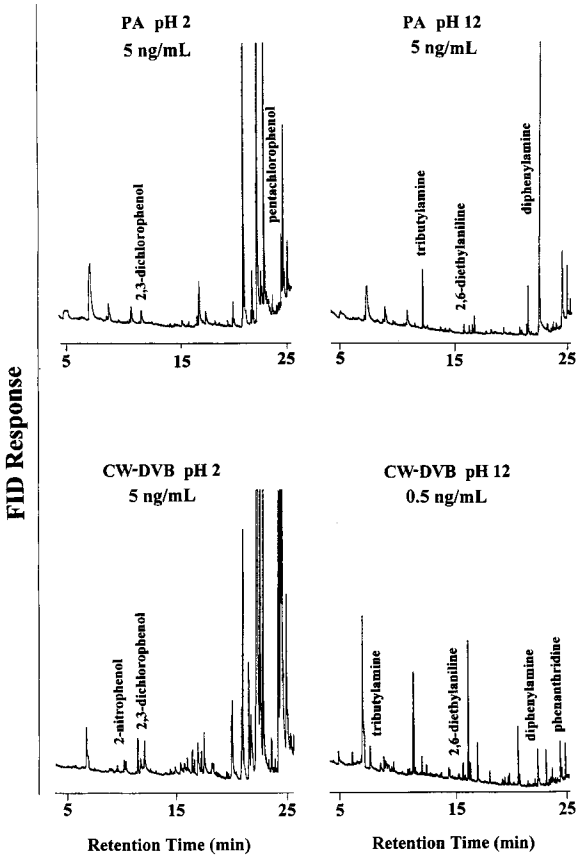

Fig. 1. GC–FID chromatograms resulting from the SPME analyses of representative organic acids (pH 2) and bases (pH 12) near their detection limit. Unidentified peaks are artifacts from the fiber sorbents. The top chromatograms were generated using a PA-coated fiber, and the bottom chromatograms were generated using a CW–DVB-coated fiber.

fibers is generally related to the K_d of the test species. However, the CW–DVB fiber has a small advantage over the PA fiber for the bases. In most cases, any large differences in detection limits (e.g., for aniline) are a result of closely-eluting artifact peaks from the sorbent material, rather than large differences in partitioning behavior.

It should be noted that GC–FID was used to determine these detection limits, and in many cases the use of a more selective and sensitive GC detector could greatly increase the method sensitivity and selectivity. For example, electron-capture detection (ECD) would be much more sensitive than FID for the chlorophenols, and would have the added advantage of not sensitively detecting the artifact peaks from the fiber sorbents.

Table 7
Experimentally-determined detection limits for a 1.9-ml water sample with flame ionization detection

	Detection limit (ng/ml)	
Compound	PA	CW–DVB
Bases (pH 12)		
Tributylamine	1	0.5
Aniline	250	5
Quinoline	50	5
2,6-Diethylaniline	5	0.5
2-Nitroaniline	10	5
Diphenylamine	5	0.5
Phenanthridine	10	0.5
Acids (pH 2)		
Phenol	50	100
2-Nitrophenol	50	5
2,3-Dichlorophenol	5	5
2,4,5-Trichlorophenol	10	10
Pentachlorophenol	5	20

A goal of this work was to utilize pH to increase the selectivity of the SPME step for organic acids versus organic bases. As shown in Tables 2–5, the use of pH to selectively extract acids versus bases works quite well with all of the fibers tested since the phenols were not normally detected in the pH 12 extractions, and the bases were not normally detected in the pH 2 extractions (with the notable exceptions of the two bases which had very low pK_a values, i.e., 2-nitroaniline and diphenylamine). However, the results in Tables 2–5 clearly demonstrate that the PA sorbent exhibits better selectivity than the CW–DVB sorbent. For example, the selectivity for phenanthridine with the PA fiber at pH 12 compared to pH 2 was ~150:1. In contrast, the selectivity for phenanthridine with the CW–DVB fiber at pH 12 versus pH 2 was only ~9:1. In addition, at a water pH of 12, 2,4,5-trichlorophenol is found in the CW–DVB extract at about 3% of the level found in the pH 2 extract, thus giving a selectivity of ~30:1. However, the minimum selectivity for the PA fiber (estimated from the FID detection limit) for 2,4,5-trichlorophenol is >500:1.

Although the CW–DVB sorbent had some advantage over the PA sorbent in detection limits, the CW–DVB sorbent was not as selective as the PA

sorbent for utilizing the water pH to extract organic acids versus bases. Therefore, subsequent studies were performed with the PA fiber.

3.3. Recoveries from surface and wastewater samples

A water sample collected from a surface wetland (a marshy area) was used for the recovery studies, since such water samples contain high levels of dissolved and suspended natural organic material, as well as suspended sediments which can interfere with sample extraction. Initial SPME with GC–FID and GC–MS analyses at pH 2 and pH 12 (prepared by adding HCl or NaOH as described above) of the water sample showed no detectable amount of the test compounds, although unidentified species eluted too close to phenol and tributylamine to allow their recoveries to be determined. Since SPME is an equilibrium, not exhaustive extraction technique, the term ''recoveries'' is somewhat ambiguous. In the present study, % recovery is defined as the concentration determined in the sample water versus the calibration standards prepared in the buffered water.

As shown in Table 8, the concentrations of both the aromatic bases and acids determined in the spiked wetland sample agreed reasonably well with the known values, with recoveries ranging from 73 to 117% of the known values. No particular trend in the recoveries of the acids or bases was observed, and the results indicate that the suspended solids in this water (~0.2%, w/w) did not substantially affect the partitioning to the SPME sorbent.

Table 8
Determination of organic acids and bases from spiked (5 μg/ml of each compound) wetlands water

Compound	% Recovery±S.D.[a]
Bases (pH 12)	
Aniline	73±19
Quinoline	117±11
2,6-Diethylaniline	103±10
2-Nitroaniline	108±8
Diphenylamine	97±13
Phenanthridine	104±9
Acids (pH 2)	
2-Nitrophenol	93±26
2,3-Dichlorophenol	93±5
2,4,5-Trichlorophenol	90±7
Pentachlorophenol	87±12

[a] Recoveries are based on quadruplicate determinations at each pH. Concentrations of phenol and tributylamine could not be determined because of interferring peaks in the GC–FID chromatogram.

Finally, the concentrations of phenols in a raw wastewater from coal gasification were determined using the SPME method and compared to the same concentrations based on four sequential methylene chloride extractions of the acidified wastewater. Since the pollutant concentrations were quite high in the raw wastewater, SPME determinations were performed on 1.9-ml samples of the water which had been diluted 1:50 in the pH 2 buffer. A comparison of the GC–FID chromatograms of the methylene chloride extracts and the SPME determinations is shown in Fig. 2. Note that several of the later-eluting species in the SPME extract are not present in the methylene chloride extract and, in general, the later-eluting species are accentuated in the SPME extract. For example, 1- and 2-naphthol are prominent in the SPME extract, but cannot be detected in the methylene chloride extract. Since these naphthols are less soluble in water than the earlier-eluting phenols, it is reasonable to expect that they would more strongly absorb to the SPME sorbent (have higher K_d values), and thus the selectivity of SPME for these compounds would be expected.

The quantitative comparisons of the conventional methylene chloride extraction and the SPME extractions are shown in Table 9. In general, the agreement between the two methods is good, and both methods show similar reproducibilities, although the SPME results from the second set of determinations had poorer reproducibilities than obtained on the first day (discussed below).

3.4. Potential problems

In addition to the SPME blank peaks discussed above and shown in Fig. 1, other potential problems may occur with SPME analyses. For example, Yang et al. [4] reported severe carryover of PCBs on the PTFE-coated stir bars used to mix water samples during SPME analyses. Fortunately, no such carryover of the test analytes occurred in our study. Incomplete thermal desorption of sorbed species from the fiber in the GC injection port also may

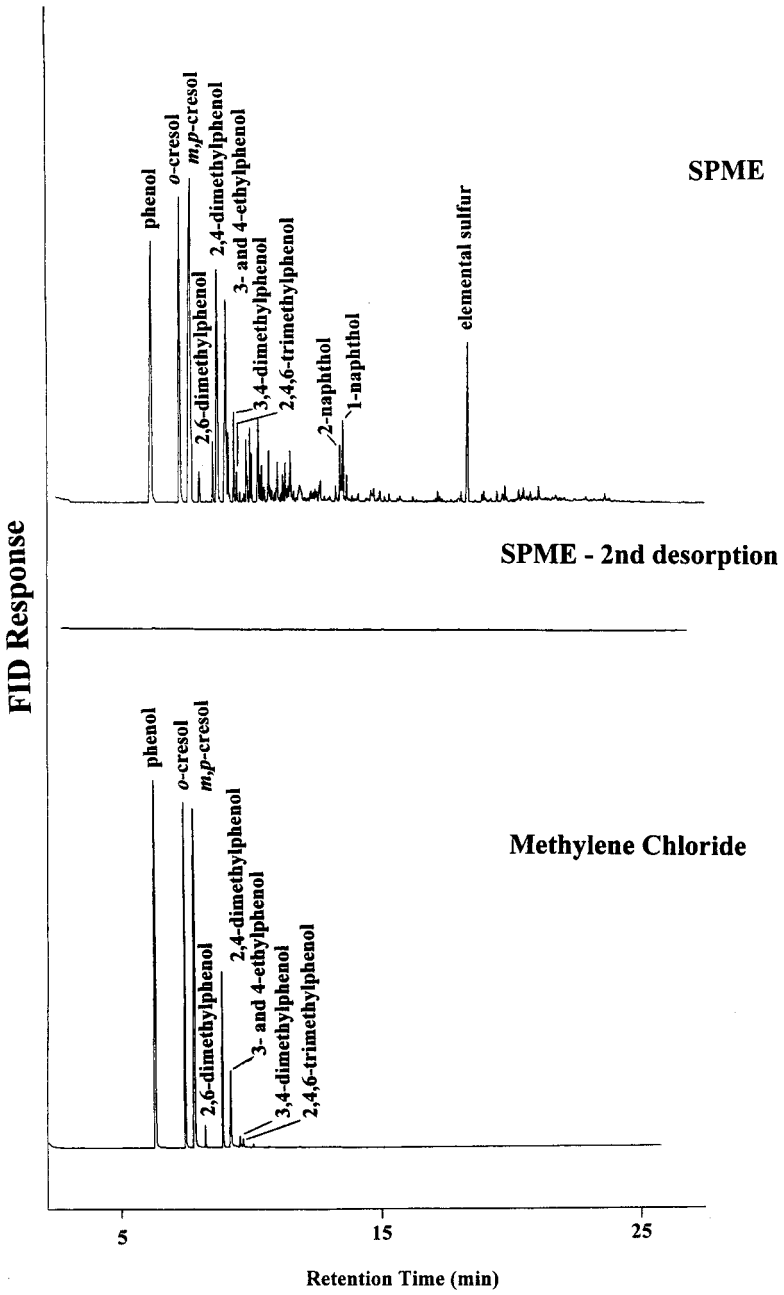

Fig. 2. GC–FID chromatograms of a coal gasification wastewater after acidification to pH 2 and extraction with methylene chloride, and SPME extraction after a 1:50 dilution in pH 2 buffer using a PA-coated fiber. A second desorbtion of the PA fiber (without cleaning) used for the SPME chromatogram (top) is shown at the same FID sensitivity (middle).

occur. For example, Buchholz [17] reported incomplete desorption of pentachlorophenol from PDMS fibers. To ensure against such carryover, two separate blanks were routinely performed throughout our study. First, fibers were frequently desorbed a second time into the GC–FID without the intermediate 10-

Table 9
Comparison of phenols in coal gasification wastewater determined using SPME and conventional methylene chloride extraction

Compound	Concentration±S.D.[a] (mg/l)		
	CH_2Cl_2 extraction	SPME (day 1)	SPME (day 2)
Phenol	1730±120	1920±20	1960±390
o-Cresol	510±30	550±20	570±130
m+*p*-Cresol	1300±90	1300±50	1370±290
2,6-Dimethylphenol	20±2	25±1	30±7
2,4-Dimethylphenol	250±20	250±10	260±60
3- and 4-Ethylphenol	260±20	220±10	230±51
3,4-Dimethylphenol	60±5	60±4	60±15
2,4,6-Trimethylphenol	5±60	5±0.4	5±1
1-Naphthol	ND[b]	7±0.4	8±2
2-Naphthol	ND	10±0.7	10±2

[a] Standard deviations were based on the analysis of quadruplicate samples by each method.
[b] ND=Not detected in the CH_2Cl_2 extract.

min cleaning step (described in Section 2.3) which was routinely applied between samples. An example is shown in Fig. 2 for the coal gasification wastewater. Second, blanks were performed using cleaned fibers with clean water (and buffer) samples using a stir bar from previous samples after cleaning as described above. Throughout our studies, both blanks remained clean, with the only significant chromatographic peaks found by GC–FID being the blank peaks from the fiber sorbents (Fig. 1).

Although the fibers in this study were generally used more than 50 times, no large degradation in the blank chromatograms were observed. However, some loss of capacity was observed with multiple uses, especially for highly-contaminated samples such as the coal gasification wastewater. For this sample, quantities of the phenols absorbed by the fiber on the second day (after five sample analyses and associated calibration runs on day 1) decreased by ~30%. Fortunately, since the decrease in fiber capacity was the same for the calibration water and the sample water, the quantitative agreement with the previous day's results was still good. However, the precision of the SPME determinations did get poorer as the fiber was used for multiple samples as reflected by the increased standard deviations for the day 2 results, compared to the day 1 results (Table 9). These results clearly suggest that any routine use of the SPME approach for complex waters should include frequent calibration runs to ensure that substantial loss of the fiber sorbent capacity has not occurred.

4. Conclusions

Adjusting the pH of water samples can be used to enhance the SPME selectivity for organic acids and bases, and sorption behavior can be predicted based on the acid dissociation constant of the solutes. Both PA- and CW–DVB-coated fibers have substantially higher K_d values for organic acids and bases than PDMS-coated fibers. CW–DVB fibers give better detection limits (typically 0.5 to 10 ng/ml) than the PA fibers (typically 1 to 50 ng/ml) using FID. However, the PA fibers give better selectivity. Frequent observation of blanks and peak areas for water calibration standards show that the fibers can normally be used for more than 50 determinations, however, the analysis of highly contaminated waters may lead to more rapid decreases in fiber capacity.

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the Agency, and no official endorsement should be inferred.

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